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Exposure of Fertilizer Mixing Plant Workers to Disulfoton

H. R. Wolfe, D. C. Staiff, J. F. Armstrong, and J. E. Davis
U.S. Environmental Protection Agency, Health Effects Research Laboratory, Field Studies Section, P.O. Box 219, Wenatchee, Wash. 98801

The systemic organophosphorus pesticide, disulfoton (O,O-diethyl S-[2-(ethylthio)ethyl] phosphorodithioate) has been used in combination with fertilizer in field soil applications for several years. Such a combination permits the farmer to apply both pesticide and fertilizer in one operation. It is often a custom blend mixed in fertilizer mixing plants to meet the specific needs of farmers. The final blend usually contains less than 0.5% disulfoton.

Initially, 10% granular disulfoton was mixed with pelletized fertilizer in a rotating drum to obtain the proper pesticide-fertilizer combination. This usually resulted in relatively dusty conditions in most work areas of fertilizer mixing plants because such structures were not necessarily designed to provide ventilation adequate to prevent excess exposure to toxic pesticides. Even though respirators were usually worn, workers occasionally complained that they felt sick from the odor of the pesticide, and they felt that their clothing was becoming impregnated with toxic material as a result of the dust in the air. This dust was probably made up of particulate material from both the granular pesticide formulation and the fertilizer pellets.

The mixing of dry granular disulfoton formulation with dry fertilizer gave way to the practice of injecting liquid concentrate pesticide into the mixing drum in a manner that evenly impregnates the fertilizer pellets, an accepted practice that has been used in recent years. Also, there has been less bagging of the mix and an increase in spout filling of broadcast dispersal trucks for bulk hauling of the mix into the field. Where the dry mix technique was discontinued in favor of the use of the liquid pesticide injection (wet mix) technique, there appeared to be much less dust in the air in the various work areas; however, the objectionable disulfoton odor was still evident, although much less so than when dry formulation was being mixed.

Although fertilizer-pesticide combinations have considerable labor saving appeal, their formulation and use is not without a few problems, including rapid degradation of the applied pesticide on certain types of fertilizers as well as the potential hazard to mixing plant workers or fertilizer-pesticide applicators (DEWEY, 1966; IBRAHIM et al. 1969). A few unconfirmed reports of illness, as well as inquiries from

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management and workers, prompted our interest in studies of exposure to the compound. The present paper reports results of studies designed to determine potential hazard to workers exposed to disulfoton during the pesticide-fertilizer mixing operation and to compare the exposure potential of the wet mix with the dry mix operations.

MATERIALS AND METHODS

Exposure studies were conducted in three plants that were considered typical fertilizer-pesticide mixing operations in the Pacific Northwest. In order to determine the potential exposure in different work situations, tests were carried out on (1) the worker who inserted the proper proportions of ingredients into the hopper where it was fed into a mixing drum (mixer), (2) the worker who filled bags with pesticide-fertilizer mix at the filler spout and removed them when full (bagger) and (3) the worker who stacked full bags of the mix onto storage pallets (stacker).

The amount of disulfoton to which a worker potentially would be subjected during work activities was estimated by the techniques and procedures described by DURHAM and WOLFE (1962). Dermal contamination was measured primarily by attaching layered-gauze absorbent pads to various parts of the worker's body or clothing and allowing them to be exposed during a timed period of work. Respiratory exposure was estimated from the contamination of special filter pads used in place of the usual outer absorbent filter pads which cover the filter cartridges of the respirators worn by the subjects. The filter pads were covered with plastic funnels modified to a specific aperture size to reproduce as nearly as possible the aerodynamics of air flow through the nostrils. The funnels also prevented direct impingement of particles onto the pad except for those carried through the apertures by respiratory action. This technique renders it unnecessary to measure total air volume, because all inhaled air passes through the filter pads.

Potential exposure calculations were based on the use of minimum protection (no respirator, shirt with short sleeves and open collar, no hat, no gloves, with the assumption that the clothing worn gave complete protection of body areas covered). This was to arrive at values that might reflect the maximum potential exposure that could occur in different work situations where proper protective gear was not utilized. However, in nearly all cases the workers wore certain protective gear items, including respirators.

Values obtained were used to calculate the milligrams of pesticide to which a worker potentially would be subjected per hour of work activity. The percent of the toxic dose to which workers were potentially exposed was calculated by the procedure described by DURHAM and WOLFE (1962), based on comparison between the dermal and respiratory exposure values determined in the present study and animal toxicity figures published by GAINES (1969).

During mixing operations air samples were taken in two general areas: (1) within 1 to 5 M of the bagging work station and (2) 8 to 10 M from all 3 main work stations. Sampling was by portable units consisting of two midget impingers connected in tandem, with vacuum supplied by battery-operated pumps and positioned 160 cm (approximately nose level) above the floor. The solvent used was 95% ethanol.

Respiratory and dermal exposure pads were extracted with benzene in a Soxhlet apparatus. These samples, as well as air sample extracts, were analyzed for disulfoton by electron-capture gas liquid chromatography. Blood samples drawn prior to and during the work season were analyzed for cholinesterase activity by the method of MICHEL (1949). Urine samples were collected from workers for attempted analysis for disulfoton metabolites by the method of SHAFIK and ENOS (1969). Attempted confirmation of that method was carried out using five adult male Sherman rats. Two were injected I.P. with a dosage of one-half the LD_{50} (6.25 mg/kg) and three were injected I.P. with a dosage of one-tenth the LD_{50} (1.25 mg/kg) of disulfoton in 0.1 ml of ethanol. Urines were collected for a 24-hour period and analyzed for O,O-diethyl phosphorothioate and O,O-diethyl phosphate.

RESULTS AND DISCUSSION

As can be seen in Table 1, potential dermal and respiratory exposure during dry mix operations was much greater than during wet mix operations. Dermal exposure during dry mix operations for all workers ranged from 0.1 to 10.5 mg/hr with a mean value of 2.0 mg/hr of work activity. Respiratory exposure ranged from 0.007 to 3.440 mg/hr with a mean of 0.325 mg/hr of work.

During wet mix operations dermal values ranged from 0.01 to 0.43 mg/hr with a mean of 0.11 mg/hr of work. Respiratory values ranged from 0.001 to 0.036 mg/hr with a mean of 0.009 mg/hr of work activity.

Results of air sampling for disulfoton during dry mix operations indicated relatively high levels as compared with levels found during wet mix operations (Table 2). Results of 11 samplings at the 1 to 5 M distance from the bagging work station showed levels from 0.001 to 2.350 mg/M^3 with a mean value of 0.633 mg/M^3 of air, and 8 samplings at the 8 to 10 M distance from the bagging station showed 0.001 to 1.000 mg/M^3 with a mean value of 0.460 mg/M^3 of air. Results of 21 samplings during wet mix operations at the 1 to 5 M distance gave levels of from < 0.001 to 0.040 mg/M^3 with a mean of < 0.006 mg/M^3 of air, and 7 samplings at the 8 to 10 M distance showed < 0.001 to 0.010 mg/M^3 with a mean value of < 0.003 mg/M^3.

TABLE 1

Potential Dermal and Respiratory Exposure of Workers to Disulfoton in Fertilizer Mixing Plants, Comparing Dry and Wet Mixing Operations

Subject	No. of exposure periods tested	Calculated exposure (mg/hr)[a]	
		Dermal	Respiratory
1. Dry mix			
All workers	21	2.0 ± 2.8	0.325 ± 0.740
Mixers	7	2.7 ± 3.5	0.656 ± 1.240
Baggers	8	1.2 ± 2.0	0.063 ± 0.065
Stackers	6	2.4 ± 2.9	0.290 ± 0.292
2. Wet mix			
All workers	20	0.11 ± 0.11	0.009 ± 0.009
Mixers	7	0.15 ± 0.16	0.013 ± 0.012
Baggers	5	0.08 ± 0.02	0.012 ± 0.008
Stackers	8	0.11 ± 0.11	0.005 ± 0.005

[a]Mean ± S.D. Exposure values calculated on the basis of no respirator, shirt with short sleeves and open collar, no gloves or hat, with the assumption that the clothing worn gave complete protection of the areas covered.

TABLE 2

Air Levels of Disulfoton in Fertilizer Mixing Plants

Distance sampler from work stations	Air level (mg/M^3)[a]			
	No. of tests	Dry mix	No. of tests	Wet mix
1-5 M from bagger	11	0.633 ± 0.645	21	0.006 ± 0.011
8-10 M from bagger, stacker, and mixer	8	0.460 ± 0.368	7	0.003 ± 0.003

[a]Mean ± S.D.

None of the values obtained for blood cholinesterase levels were below the low normal values of 0.39 and 0.44 ΔpH/hr for red cells and plasma, respectively, as reported for the general population (HAYES, 1963); however, some of the workers involved in the dry mix operations did show a gradual decrease with time of exposure in their red cell values. These might have dropped to a level below their normal range if their exposure period had extended more than 9 weeks. It was difficult to obtain many pre-exposure cholinesterase values because it was necessary to rely on routine blood sampling by private physicians, as requested by the mixing plants, before we could obtain samples for analysis. In many cases men were hired and exposed to disulfoton for a week or two before bloods were drawn. Based on 47 blood samples analyzed, and assuming that values for samples drawn two weeks after they started work were near pre-exposure levels, red cell cholinesterase values for dry mix workers were depressed an average of 22.8% after 9 weeks. No similar trend was exhibited for either red cell or plasma cholinesterase for wet mix workers.

Attempts to detect metabolites in 152 urine samples collected from exposed workers were unsuccessful. Data on excretion in urine would have provided some information on the amount of pesticide actually absorbed. At the time the urine samples were being analyzed we were surprised that metabolites were not detected in at least some of the samples. The simple recovery experiment on rats, carried out in an attempt to explain the negative results, showed that rats dosed I.P. with either one-half or one-tenth of an LD_{50} of disulfoton excreted a total of only 3% of the dose as O,O-diethyl phosphorothioate and O,O-diethyl phosphate, which are the only metabolites detectable by the method of SHAFIK and ENOS (1969) in urine collected during a 24-hour period. Since most of the absorbed disulfoton may result in metabolites that are not detected by this analytical procedure, it is not surprising that we were not able to find detectable levels in the worker's urine.

During dry mix operations potential dermal exposure values for mixers and stackers were approximately the same, both being somewhat higher than for baggers. Respiratory exposure values were relatively high for mixers and relatively low for baggers. The higher dermal and respiratory values for mixers was expected because of the practice of dumping dry granular 10% disulfoton formulation into the mixing hopper by hand, which included cutting the paper sacks open and shaking out the last bit of contents. The fact that potential exposure, and especially respiratory exposure, of stackers was higher than for baggers was not expected, based on our observations in conventional pesticide formulating plants. We did observe that, where dry mix was involved, there was often a puff of dust from creases or seams on the filled bags as the stacker placed them on the storage pallet. Apparently this produces more dermal and respiratory exposure than the bagger receives at his work station. In fact, the mean value for potential respiratory exposure of stackers was approximately four times that for baggers; however, their potential respiratory exposure was only approximately one-tenth that of the mixers who were more closely associated with the concentrated 10% granular formulation. Exposure of baggers and stackers was primarily to the mixed formulation containing less than 0.5% disulfoton.

Values obtained for wet mix operations indicate that the switch from the dry mix practice to wet mix operations produced a dramatic reduction in both dermal and respiratory exposure of workers. Mean value for dermal exposure to all workers was about 18 times less than that obtained for dry mix operations and the mean value for respiratory exposure was approximately 36 times less than during dry mix operations. The reduction of visible dust near the test work areas and in ambient air in other areas of the plant building was apparent. This was undoubtedly due to the wetting effect that resulted from impregnation of the fertilizer granules by the liquid concentrate pesticide. As can be seen in Table 1, dermal exposure values for baggers were slightly lower than for mixers and stackers. Lowest respiratory values were for stackers, which is understandable because little, if any, dust could be observed coming from creases or seams of the filled bags while they were being stacked onto pallets, as was the observation where dry mix was involved. There was considerable variation in the range of exposure values for each work activity. Such variations may be due to several factors including worker carelessness and bagging equipment malfunction.

If all the disulfoton indicated by the highest potential dermal and respiratory values obtained for dry mix operations (10.5 mg/hr dermal and 3.4 mg/hr respiratory) were to be completely absorbed by a worker, he would be subjected to approximately 4.3% of a toxic dose per hour of exposure, based on minimum protection as described earlier. Using average values for this operation (2.0 mg/hr dermal and 0.32 mg/hr respiratory) the worker would be subjected to only 0.5% of a toxic dose per hour.

During wet mix operations the high values (0.43 mg/hr dermal and 0.036 mg/hr respiratory) reflect approximately 0.4% of a toxic dose per hour of exposure while average values for all workers (0.11 mg/hr dermal and 0.009 mg/hr respiratory) indicate only 0.02% of a toxic dose.

The fact that the highest values obtained (dry mix operations) indicate potential absorption of around 34.4% of a toxic dose per 8-hour work day points out that relatively high exposure can occur. This emphasizes the importance of following safety precautions to prevent excess exposure, especially when working with dry formulations. Apparently not all of the pesticide that impinges on exposed skin areas is absorbed, otherwise more illnesses or indications of severe cholinesterase depletion would have been reported by now. Also, the use of protective gear has undoubtedly reduced exposure.

A REPORT OF THE 1975 JOINT MEETING OF THE FAO WORKING PARTY OF EXPERTS ON PESTICIDE RESIDUES, AND THE WHO EXPERT COMMITTEE ON PESTICIDE RESIDUES (1976) indicates that the estimated acceptable daily intake of disulfoton for man is 0.002 mg/kg per day. For a 70 kg man this would be 0.14 mg per 8-hour work day. All daily exposures determined in this study, except a few of the lowest values for wet mix operations, were above that level.

The exposure values obtained during the experiment do not reflect any of the unusual exposure situations that do occur on rare occasions. These include accidental skin contact with the liquid concentrate disulfoton during wet mix operations when connecting barrels of liquid pesticide to the closed system used to inject disulfoton into the fertilizer mixing drum, or, in rare cases, during handling of bags of the mix where the wrong type of fertilizer is coated and the pesticide bleeds off into the paper sack material and penetrates to the surface. One incident of poisoning due to such "bleed-off" was brought to our attention.

It is of interest that levels of disulfoton in all of the air samples collected during dry mix operations, except three, exceeded the 0.1 mg/M^3 threshold limit value established for disulfoton by the AMERICAN CONFERENCE OF GOVERNMENTAL INDUSTRIAL HYGIENISTS (1976) as an airborne concentration under which it is believed workers may be repeatedly exposed without adverse effect. However, none of the samples collected during wet mix operations exceeded that level. This clearly points in favor of wet mix operations as far as hazard from routine daily exposure is concerned. We rarely observed individuals at main work stations who were without approved respiratory protection. This may be one of the main reasons why blood cholinesterase levels of workers in either dry or wet mix operations were, in most cases, not appreciably lowered during the comparatively short mixing season which, in the northern portion of the country, usually runs from late February or early March through May. In other areas where the mixing season may be longer, blood cholinesterase levels of workers who have been on the job for over three months should probably be given special attention.

Although dermal and respiratory exposure may be relatively low during normal wet mix operations, this does not minimize the need for exceptional care during the handling or hookup of liquid concentrate disulfoton to the mixing drum injection system. In fact, the potential for heavy accidental exposure may be greater during such activity than during dry mix operations. This emphasizes the need to avoid becoming lax in following safety precautions. However, with increased attention being given to worker safety nowadays, along with an apparent trend toward less mixing of disulfoton with fertilizer, illnesses resulting from exposure to that compound during mixing operations should be few, if any, in the future.

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